FORMATION CONSTANT DETERMINATIONS FOR SOME 2-ALKYLAMINOPYRIDINE N-OXIDES WITH FERRIC ION IN METHANOL

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ABSTRACT The complexes of various alkylaminopyridine N-oxides with ferric ion have been studied. In alcoholic solution, 1:1 and 3:1 (ligand:metal) species are found as determined by calculated formation constants. The steric bulk of the alkyl groups appears to influence the formation of the 1:1 species, but is of less importance for the 3:1 species.

There have been numerous reports including the review articles of Garvey (1969) and Karayannis (1973) concerning the preparation and characterization of metal ion complexes of pyridine N-oxides. However, there have been few reports on the formation constants of these metal ion complexes in solution. Formation constants of 2-aminopyridine N-oxide with a number of dipositive metal ions in dioxane-water mixtures have been reported by Sigel (1963).

The ferric ion, often used as a qualitative color test reagent for the N-oxide function, yields blue solutions with many of the 2-alkylaminopyridine N-oxides and lends itself to a spectrophotometric determination of formation constants. Because color tests are most often carried out in alcoholic solution, we selected methanol as the solvent for our initial studies.

EXPERIMENTAL

Weighed amounts of vacuum dried $Fe(ClO_4)_3 \cdot 6H_2O$ were dissolved in 9:1 (by volume) methanol:dimethoxypropane to give a stock solution of 1×10^{-2} M. The stock solution was placed in a refrigerator in a foil-wrapped container and all ferric ion solutions were prepared from this solution by dilution with methanol. The 2-alkylaminopyridine N-oxides were prepared by the method described by Katritzky (1957) and dissolved in methanol to the desired concentration. A series of solutions with constant ferric ion concentration and varying N-oxide ligand concentrations were prepared and allowed to come to thermal equilibrium in a constant temperature bath. The concentration ratio of ligand:metal ion was varied from 0.1:1 to 20:1. The absorption spectra were measured in one cm silica cells from 700 nm to 400 nm on a Cary 14 Recording Spectrophotometer equipped with a constant temperature cell compartment and cell holder (±0.2 deg). Absorbances at 650, 610, 590, 570, and 540 nm for each sample (a typical experiment involved more than twenty samples) were analyzed by means of the computer program Spectro - 1130 of Magnell (1973). The values of the formation constants and extinction coefficients shown in Table 1 are the average of at least three different experiments having different ferric ion concentrations. A ferric ion concentration of 2×10^{-4} M and variation of the ligand concentration from 2×10^{-5} M to 1×10^{-3} M illustrates the nature of solutions used in this work.

RESULTS AND DISCUSSION

In Table 1 values for β_1 and β_3 are reported where

$$\beta_1 = \frac{[FeL^{3+}]}{[Fe^{3+}]\,[L]} \qquad \text{and} \qquad \beta_3 = \frac{[FeL_3{}^{3+}]}{[Fe^{3+}]\,[L]^3}$$

and $[L]$ represents the concentration of a 2-alkylaminopyridine N-oxide. Values for the intermediate β_2 are not reported because we were unable to establish the existence of $FeL_2{}^{3+}$ by plotting the absorbance vs. $[L]$ (at constant $[M]$) for the different wavelengths. In addition, its inclusion in the data input at the expected values (e.g.10^{10}) did not allow the program to converge. The reasons for this may simply be a low molar absorptivity for $FeL_2{}^{3+}$ such that its presence is masked by the two more strongly absorbing species, FeL^{3+} and $FeL_3{}^{3+}$. The existence of a 1:1 species is analogous to our observations of the 2-mercaptopyridine N-oxide Fe^{+3} system which forms a blue 1:1 and a violet 3:1 species. In both cases a 1:1 species is formed which has an absorption maximum at longer wavelength than the 3:1.

The nature of the ligand (the alkyl substituent) plays a significant role in the magnitude of formation constant values. With increasing size of the alkyl moiety there is a decrease in the magnitude of β_1 which must be due to steric hindrance. The values for β_3, however, do not show the same trend, the 2-benzylaminopyridine N-oxide value for β_3 being higher than the corresponding value for the ligand substituted with one ethyl group. Apparently, the ability of the substituents to provide an inductive electron donating effect is more important than a steric effect. We assume that the ligands retain the amino proton in each example upon complexation as was observed by Kohrman (1975) in the isolation of complexes of 2-methylaminopyridine N-oxide.

Attempts to determine thermodynamic parameters by variation of temperatures from 5°C to 40°C proved ineffective. Variations in β's were irregular and within experimental error as reported in Table 1.

TABLE 1

Formation Constants of Fe^{3+} Complexes with 2-Alkylaminopyridine N-Oxides at 25°C.

N-oxides (L)	Formation Constants	Molar Absorptivity*				
		540nm	570nm	590nm	610nm	650nm
2-methyl	$\beta_1 = 2.32\times10^5 \pm .86\times10^5$	657	811	962	1082	1191
	$\beta_3 = 3.54\times10^{14} \pm 1.9\times10^{14}$	2742	3248	3329	3163	2321
2-ethyl	$\beta_1 = 1.64\times10^5 \pm .64\times10^5$	372	503	607	707	757
	$\beta_3 = 1.24\times10^{14} \pm .7\times10^{14}$	2398	2818	2948	2958	2176
2-octyl	$\beta_1 = 8.70\times10^4 \pm 1.31\times10^4$	158	232	291	328	367
	$\beta_3 = 1.07\times10^{13} \pm .32\times10^{13}$	2156	2544	2642	2538	2056
2-benzyl	$\beta_1 = 8.79\times10^4 \pm 4.4\times10^4$	545	682	746	771	642
	$\beta_3 = 2.30\times10^{14} \pm 1.5\times10^{14}$	2583	2939	2995	2815	1988

*The calculated error in the molar absorptivities is less than 8% for the 1:1 complexes and less than 2% for the 3:1 complexes.

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LITERATURE CITED

GARVEY, F. G., J. H. Nelson and R. O. Ragsdale. 1968. The Coordination Chemistry of Aromatic Amine N-Oxides. Coord. Chem. Rev., 3:375-407.

KARAYANNIS, N. M., L. L. Pytlewski and C. M. Mikulski. 1973. Metal Complexes of Aromatic Amine N-Oxides. Coord. Chem. Rev., 11:93-159.

KATRITZKY, A. R., 1975. The Structure and Reactivity of 2-Aminopyridine 1-Oxide. J. Chem. Soc., 191-197.

KOHRMAN, R. E., P. G. Phadtare and D. X. West. 1975. Metal Ion Complexes of 2-Methylaminopyridine N-Oxide. J. Inorg. Nucl. Chem., 37:301-303.

MAGNELL, K. R., 1973. Formation Constants of Multi-Specie Equilibria from Spectrophotometric Data Using Small Computer Systems. J. Chem. Educ., 50:619.

SIGEL, H. and H. Brintzinger. 1963. Metallionen-Komplexe von 2-Aminopyridin-1-oxid. Helv. Chim. Acta, 46:701-712.